SYNOPSIS FOR Ph.D. PROGRAMME

TREATMENT OF WASTEWATER BY NANOPARTICLES SYNTHESIZED USING AGRO-WASTE

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INTRODUCTION

Water is the largest part of essential natural resource for existence of life on earth and a source of evolution of human civilization. Water is known as universal solvent and it easily dissolves other substances (Sushma &Richa, 2015). Water contamination is a major globally problem and the growing utilization of limited water resources creates a need for efficient purification methods (FAO, 2003). Contaminated water contains unwanted substances and it adversely affects the quality making it unsuitable for use. Water resources become contaminated from various sources such as residential areas, commercial, industrial practices, agricultural practices etc. The characteristics of waste water vary widely and depend upon the source from which it is generated (Sulekha, 2016). The problem of water pollution is getting very severe, especially in developing countries with disposal of untreated/ partially treated waste water. This disposal has resulted in additional load of inorganic, organic and microbial pollutants which further deteriorates the water quality. It is necessity to control the harmful effects of contaminants and improve the human living environment. The need for contaminant removal has become imperative (Hung *et al*., 2010; Pang *et al.,* 2011a). Conventionally, the pollutants from wastewater are removed to a certain extent in wastewater treatment facilities (Obald *et al.*, 2016). The conventional wastewater treatment processes are not able to address effective removal of a wide spectrum of toxic chemicals and pathogenic microorganisms in raw water. This is the right time to address this problem and researchers need to develop advanced technologies which are cost effective, durable and more efficient as compared to existing treatment option. Several physicochemical treatment techniques have been investigated by scientists and researchers for the removal of different types of impurities from wastewater such as membrane filtration, chemical reduction, adsorption/biosorption, ion-exchange, coagulation-flocculation, chemical precipitation, flotation, photocatalysis, ozonation, sonication and electrochemical method like electrodialysis. Comparatively, adsorption as an exception is the most effective and widely used technique of waste water treatment due to higher output and lower cost of adsorbents (Khandanlou, *et al*., 2015).

In recent years, Nanotechnology has emerged as cutting edge technology with interdisciplinary applications in the field of physics, chemistry, material science, environmental sciences, biology and medicine. Recently application of nanotechnology is increasing in wastewater treatment. Nanomaterials are typically defined as materials smaller than 100 nm in at least one dimensional. At nano scale, materials possess some new size-dependent properties such as large surface to volume ratio, reactivity, rapid dissolution and adsorption which are better compared to the bulk material (Sushma & Richa, 2015**)**.

Various processes are used for nanomaterials synthesis such as physical, chemical and biological. These physical and chemical processes are used for various shapes, sizes, monodisperse, mesoporous and fast growing nanomaterials (Galal *et al.*, 2013). Biological material microorganism like bacteria, fungus, algae etc. and plant leaf extract contain antioxidants or reducing compounds for nanomaterial synthesis. Nanomaterials are synthesized in different shape or structure like nanotube, nanowire, nanoflower, nanorod, nanosphere, nanosheet, nanobelt etc. and size i.e. 1 nm to 100 nm.

The application of nanomaterials in waste water treatment has drawn wide attention and due to their small sizes and thus large specific surface areas, nanomaterials have strong adsorption capacities and reactivity. Moreover the mobility of nanomaterials in solution is high. Heavy metals, organic pollutants, inorganic anions and bacteria have are reported to be successfully removed by various nanomaterials. On the basis of numerous studies, nanomaterials show great promise for application in wastewater treatment. At present, the most extensively studied nanomaterials for wastewater treatment mainly include zero-valent metal nanoparticles, metal-oxide nanoparticles, carbon nanotubes and nanocomposites.

At present time, the use of nanomaterials are increasing for wastewater treatment because the traditional adsorbents treat wastewater with low adsorption capacities and efficiencies. Compared with traditional materials nano-structure adsorbents have exhibited much higher efficiency and faster rates of pollutant removal in wastewater treatment. Nanomaterials used as adsorbents for wastewater treatment should satisfy the following criterions (a) the nano-adsorbents themselves should be non-toxic (b) the adsorbent should have relatively high adsorption capacities and selectively to the low concentration of pollutants (c) the adsorbed pollutant should be removed from the surface of the nano-adsorbent easily. Apart from surface-adsorption of micro-pollutants over the used nano-adsorbent, some of the metal-based nanomaterials have catalytic oxidation properties. Application of nano TiO_2, nano zero-valent iron (NZVI) and nano-zinc oxide has been found useful in catalytic oxidation of organic impurities (pesticides, hydrocarbons, organic halogens etc.) at degradation rate placed significantly above the rate of secondary wastewater treatment. Capping of such nano catalysts with suitable oxidizing agents extracted from agro-based material may further enhance its properties towards mineralization of organic pollutants.

Present research will be aimed to treat the waste water under lab conditions using nanoparticles prepared at Lab Scale using agro-waste like rice husk, wheat straw etc. First of all metallic nanoparticles will be prepared by using plant extracts of different agro waste and then efficacy of wastewater treatment of these metallic nanoparticles will be evaluated in terms of removal of COD, ammonia, phosphate, nitrate etc.

REVIEW OF LITERATURE

The problem of water pollution is getting severe with disposal of untreated waste water. It's necessary to confirm that pollutants remove from waste water before its discharge into water. In this situation nanotechnology is a new emerging and interesting field of science regarding water purification. It offers potential benefits like low cost, reuse and extremely economical in removing and recovering the pollutants. Nanomaterials synthesized by physical, chemical and biological process but biological approaches using agro-waste for synthesis of nanoparticles are less toxic. In past many researchers have performed their works on synthesis, characterization and application of the nanoparticles. The synthesis of nanoparticles are done by various methods some of them are chemical co-precipitation method (Khandanlou *et al.,* 2015), sol-gel method (Le *et al.,* 2013), calcination and microwave assisted method (Herlekar and Barve, 2015). Due to their disadvantages such as their ill effect on environment leads to the discovery of new and better methodology of synthesis of nanoparticles called green method. In this method different parts of the plants and plant extracts such as leaves, fruits, flowers, straw and husk etc. are used as reducing agents. There have been many reports of the synthesis of the nanoparticles with the help of eucalyptus leaf extract (Wang *et al.*,2013), turmeric leaf (Obald *et al.,* 2016), neem leaf (Devatha *et al.*,2016), rice straw, rice husk (Ghorbani *et al.*,2015), wheat straw (Pirbazari *et al.*,2014), coconut shell (Sophia *et al*., 2011). A brief review of such studies is presented in this section.

Rice husk and coconut shell used as a bio-reducing agent to synthesize carbon. Carbon was found self sufficient to remove 99% E.coli. from waste water (Sophia *et al*., 2011). Fe nanoparticles synthesized by Eucalyptus leaf extracts removed 71.7% total N and 84.5% COD from swine waste water (Wang *et al.*,2013).

Herlekar *et al.*,(2014) highlights the recent developments in iron and arsenic nanoparticles synthesis by eco-friendly techniques and their application in the field of environmental remediation. Magnetic nanocomposites (Fe_3O_4 NCs) nanoparticles synthesized using rice straw by co-precipitation method has observed 96.25% removal of Pb (II) and 75.54% removal of Cu (II) from aqueous solution (Khandanlou *et al.*, 2015). Magnetic nanoparticles synthesized using turmeric leaves by calcination and microwave assisted method resulted in 82% removal of PO_4 and 83% removal of COD from sewage at optimum condition (Herlekar and Barve ,2015). Agro-waste based activated carbon remove 100% As (V) from polluted river water (Pirila, 2015). CuO nanoparticles removed total coliform (TC), fecal coliform (FC) and *Enterococcus faecalis* 76% to 85% from waste water by using tetraoctylammonium bromide (TOAB) and more than 92% without tetraoctylammonium bromide (TOAB) (Suleiman *et al.*,2015). Iron oxide nanoparticle and rice husk ash in combination removed 99.7% Cr from sewage (Asrari and Nia, 2016). Deokar *et al.*, (2016) studied the removal of 2, 4 - dichlorophenoxyacetic acid from aqueous solution by using rice husk ash and baggase fly ash. They found that carbon content controls the adsorption capacity and silica controls the kinetics. Fe nanoparticles synthesized by using *Azadiracta indica* for removal of phosphate, ammonia nitrogen and COD from domestic waste water. They removed 98.08% phosphate, 84.32% ammonical nitrogen and 82.35% COD from domestic waste water (Devatha *et al.*, 2016). Magnetic mesoporous silica of magMCM-41 synthesized using amorphous silica from rice husk and lead to 60.25% removal of Cd (II) from aqueous solution (Kamari and Ghorbani, 2016). Fe nanoparticles synthesized using Turmeric leaves by calcination and microwave methods. Fe nanoparticles removed 90%, 92% and 95% of Orthophosphate, Chemical Oxygen Demand and *Escherichia coli* respectively from domestic waste water (Obald *et al.*, 2016). Rice husk and saw dust powder removed 80% iron

from synthetic waste water (Akiladevi *et al*., 2017). Wheat straw biochar supported nanoscale zero-valent iron removed 92% trichloroethylene (TCE) at pH 5.2 from contaminated groundwater (Hui Li *et al.,* 2017). Nano alumina (NA) and activated charcoal (AC) have been used for removal of phosphate from aqueous waste water and observed 90.2% PO_4 removal in 120 min at pH 6 and 3.2 g/L activated charcoal dosage. When nano alumina was used at dosage of 1.6 g/L, PO_4 removal was reached to 100% in 90 min at pH 6 (Mor *et al*.,2017). Zinc Oxide nanoparticles removed 100% total coliform bacteria from municipal activated sludge effluent in concentration of 1.1 g L^{-1} in 90 min contact time (Mostafaii *et al.,*2017).

The studies on environmental application of nano-materials in wastewater treatment are either carried out on commercially available materials or on other metals which are not in nano-range *w.r.t.* size. Most of the studies on application of metal-based nanomaterials have been carried out either synthetic wastewater, or these deal with a single pollutant e.g. organic matter (in terms of BOD/COD), nitrogen, phosphate, heavy metal etc. A comprehensive study on effective treatment of waste water for the diversity of pollutants (organic/inorganic; toxic/non-toxic; in bulk/trace; conventional/emerging etc.) is missing. Moreover, identifying the strengths and weaknesses associated with each treatment technology and overcoming it with different sets of permutations and combinations to finally arrive at a treatment process which is most effective; least polluting; universally-applicable; cost-effective; and environment-friendly is seldom being done. In the present study, we propose to combine highly efficient advanced oxidation processes (AOPs) with recent subject of nanotechnology aiming the effective utilization of agricultural waste simultaneously. Therefore, the present study is undertaken with the following objectives

OBJECTIVES:

- Synthesis of metallic nanoparticles using agro-waste and their characterization.
- Optimization of operating parameters such as pH, temperature, contact time, nanoparticle dosage etc. for different AOPs (Advanced oxidation processes) using nanoparticles.
- Development of an effective treatment scheme for wastewater treatment.

RESEARCH METHODOLOGY:-

1. **Synthesis of nanoparticles by using agro-waste.**

   Different types of agro-waste will be used for synthesis of nanoparticles using different techniques.

2. **Characterization of nanoparticles.**

   The characterization of any material is essential to have the recoverability of the results. Shape, particle size, molecular structure, surface area and functional group present in nanoparticles will be characterized using FTIR (Fourier transform infra-red spectroscopy), SEM (Scanning electron microscopy), TEM (Transmission electron microscopy).

3. **Optimization of operating parameters for different AOPs:**

   (a)Photocatalysis: The photocatalytic oxidizing capacity of synthesized nanoparticles will be optimized on the basis of dose of photocatalyst, pH, type of light (solar/ UV), wavelength and intensity of light for treatment

of wastewater. Effect of addition of H_2O_2 along with the photocatalyst will also be tested.

(b)Photo- Fenton: The Photo-Fenton process shall be optimized for parameters like dose of ferrous ions (Fe^{2+}), concentration of H_2O_2 , pH during treatment, Fe^{2+} / H_2O_2, type of light (UV/ solar) etc. using nanoparticles for wastewater treatment.

(c)Sonication: The optimization of degradation during sonication shall be done at different of sonication, temperature and presence/absence of light for wastewater treatment with the help nanoparticles. In all treatment the AOPs efficiency for removal of different pollutants like nitrate, phosphate, ammonia and COD for wastewater will be studied.

4. Application of nanoparticle for pollutants removal from wastewater.

Depending upon the results obtained for above study, an effective treatment scheme for treatment of wastewater will be developed.

FUTURE PROSPECTIVE AND SIGNIFICANCE:-

Due to population explosion the demand of safe drinking water and as well as wastewater generation has increased tremendously in past few decades. Due to presence high organic and inorganic pollutants and pathogenic organisms in wastewater, its disposal without treatment has adversely affected the environment especially our rivers. That's why, the treatment of wastewater is essential before its disposal. The various conventional methods for wastewater treatment are present but they are costly, non-economical, generation of toxic ordure and complicated procedure involved in the treatment. The advanced new green technological methods are being introduced to overcome the conventional methods of wastewater treatment i.e. Nanotechnology. Nanotechnology revolution will play an essential role in solving the problem of rising demands of clean water. Nanomaterials have unique characteristics for example small particle size (1 nm to 100 nm), high surface area to volume ratio, surface charge, high thermal stability and magnetic property that make them particularly attractive for wastewater treatment applications such as disinfection, adsorption and membrane separations. Nanomaterials of various shape and size can be synthesized by physical and chemical process but these are non-ecofriendly. Biological approaches using agro waste for synthesis of nanoparticles have been suggested as valuable alternative to physical and chemical

methods. In comparison to engineered nanoparticles few studies confirm that biosynthesized nanoparticles are less toxic.

In recent years, the quantity of agro waste has been rising rapidly all over the world. Near about 350 million tonnes of agro waste is generated every year in India alone and near about 998 million tonnes globally. The agro waste is almost 80% of the biomass on the agricultural fields and is often burnt in fields resulting in large amount of greenhouse gas emissions and also problems like smog resulting in serious health problems. Therefore there is a need to adopt proper approaches to reduce and reuse agro waste.

The use of agro waste for nanoparticle synthesis is comparatively new and under researched technique. Synthesis of nanoparticles using agro waste is very cost effective, so can be used as an economic and valid alternative for the large scale production of nanoparticles. In this study efforts will be made to develop some nanoparticles having above stated properties using different agro waste applying the principles of green chemistry. The newly developed nanoparticles will be tested for their adsorption efficiency for contaminants removal from wastewater. If some nanoparticles were found to have significant adsorption efficiency, then may be very useful to control water pollution in future.

YEARLY PLAN OF WORK

1st year plan

- Literature review
- Collection of agro-waste samples

2nd year plan

- Optimization of various parameters for synthesis of nanoparticles
- Selection of nanoparticles
- Characterization of nanoparticles by FTIR, SEM, TEM

3rd year plan

- Application of nanoparticles for wastewater treatment
- Compilation of research findings and interpreting results
- Thesis writing

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